

Article

Substituent Effects in Weak Charge-Transfer Cocrystals of Benzene Derivatives with Classical TCNQ Acceptors: Experimental and Theoretical Study

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Abstract: A series of xylene charge-transfer complexes with fluorine-substituted tetracyanoquinodimethane (TCNQ) acceptors were studied experimentally and theoretically in order to reveal the role of various intermolecular interactions on stoichiometry and the crystal structure. It was shown that *o*-xylene face-to-face donor–donor interactions became significant enough to result in the formation of 2:1 cocrystals with F₁TCNQ and F₄TCNQ irrespective of growth conditions. The supramolecular arrangement in these cocrystals is mainly determined by the number of fluorine atoms in the acceptor. Comparative DFT and MP2 calculations of the pairwise intermolecular interactions revealed the overestimation of the dispersion energy for these systems by the DFT-wB97XD approach.

Keywords: charge-transfer cocrystals; fluorine-substituted TCNQ acceptors; quantum chemical calculations; dispersion interactions



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1. Introduction

Organic charge-transfer (CT) cocrystals continue to attract attention in view of their increasing use in molecular electronics and wide opportunities to create diverse materials by variations in donor and acceptor components [1–6]. Obviously, the properties of cocrystals are determined by the molecules that constitute the material [7–10], but even more important is the supramolecular arrangement of coformers in cocrystals and the intermolecular interactions, which evoke new properties, not inherent to individual compounds [1]. Thus, the key points involve the control over the crystal structure and the understanding of the “structure-property” relationship. To gain this control one should take into account multiple factors: the electronic structures of donor and acceptor molecules, the fit between their boundary electronic orbitals, the relative dimensions of coformers, the complementarity of the forms and shapes, growth conditions, etc.

Strong donors, such as polycyclic aromatic hydrocarbons (PAH), readily form cocrystals with strong acceptors from the TCNQ family. A good illustration of strong CT cocrystals are complexes of tetracene with TCNQ, F₂TCNQ and F₄TCNQ [11–16]. Two combinations, tetracene/TCNQ and tetracene/F₄TCNQ, involve components of comparable size that form cocrystals with mixed donor–acceptor stacks via strong CT interactions. However, the crystal structure of these two CT complexes is completely different. This is due to the different ability of the acceptor molecules in side-on interactions. The presence of hydrogen atoms in the TCNQ and F₂TCNQ molecules promotes intermolecular C–H...N hydrogen bonds between the acceptors. Meanwhile, the substitution of hydrogens by fluorine atoms increases the acceptor properties of the TCNQ derivative, but more importantly, it promotes acceptor–donor F...H lateral interactions, which results in completely different supramolecular arrangements due to the different directionalities of the involved

interactions: a layered structure for the complex with TCNQ and herringbone packing for the cocrystal with F₄TCNQ.

Another demonstrative example is a series of cocrystals with a picene molecule as the donor and TCNQ [17], F₂TCNQ [17] and F₄TCNQ [18] as the acceptors. This series of acceptors is also prone to different lateral interactions; however, the crystal structure is dominated by the greater geometrical dimensions of picene compared with the acceptor molecules, and this factor prevents the latter from acceptor–acceptor interactions. Thus, this series of complexes form isomorphous crystals with similar unit cell dimensions and the same herringbone packing.

A more complicated scenario can be observed for very small donor aromatic molecules and classical TCNQ acceptors. This combination can produce ambiguous results in terms of crystal structure. The reasons for this are the very weak CT face-to-face interactions due to the small size of the donor, and multiple lateral interactions, which are possible with the participation of the acceptors. They strongly depend on the number of fluorine and hydrogen atoms in the acceptor coformer. The smallest aromatic benzene molecule does not form cocrystals with the TCNQ derivatives judging by the absence of reliable data in CSD [19]: only one entry (refcode TCNQBZ) without coordinates is present. However, benzene-containing cocrystals are numerous for three-component systems. In the majority of cases, benzene participates in C–H... π interactions with PAH donors with a nearly orthogonal orientation of the aromatic planes [20–22]. The introduction of the methyl group increases the donor properties of benzene and allows a series of toluene CT cocrystals with TCNQ derivatives demonstrating weak face-to-face π – π interactions [23,24] to be obtained. The methyl substitution shows up not only in the increase in the donor properties of the aromatic molecule, but can also result in a completely different crystal packing as occurs in the complexes containing anthracene versus methylanthracene donors with TCNQ acceptors [25].

Herewith, we continue to study the structure and interactions in weak CT cocrystals with substituted benzenes as donors and present the results for xylene cocrystals with TCNQ and its fluorine-substituted derivatives, keeping in mind a dual objective: to reveal the main factors that determine the supramolecular arrangement in cocrystals of small donors with classical acceptors and to check the applicability of various quantum chemical approaches for the analysis of intermolecular interactions.

2. Materials and Methods

2.1. Crystal Growth

The following commercially available reagents were used: 2-fluoro-7,7,8,8-tetracyanoquinodimethane (F₁TCNQ) (98+%, TCI); 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane (F₂TCNQ) (98+%, TCI); tetrafluorotetracyanoquinodimethane (F₄TCNQ) (98+%, TCI); *o*-xylene (98%, SRL); *p*-xylene (99%, SRL).

Preparation of 2-fluoro-7,7,8,8-tetracyanoquinodimethane, 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane and tetrafluorotetracyanoquinodimethane cocrystals (*o*-xylene/F₁TCNQ (1), *o*-xylene/F₂TCNQ (2), *o*-xylene/F₄TCNQ (3), *p*-xylene/F₁TCNQ (4)). F₁TCNQ (6 mg, 0.027 mmol), F₂TCNQ (6 mg, 0.025 mmol) and F₄TCNQ (6 mg, 0.022 mmol) were placed in test tubes with screw caps. Then 2 mL of *o*-xylene (for all acceptors) and 2.5 mL of *p*-xylene (only for F₁TCNQ) were correspondingly added and all tubes were heated at 130 °C until the starting compounds were completely dissolved. Cocrystals were grown by keeping the resulting solutions at room temperature with slow solvent evaporation (up to ~1/4 of the original volume).

Drying of the *o*-xylene/F₁TCNQ cocrystals in vacuo leads to their discoloration (presumably because of the destruction of the complex due to evaporation of the solvent), so all cocrystals after filtration were placed in Fomblin for further study of their molecular structure by X-ray single crystal diffraction.

A similar method was applied to grow the cocrystals of *p*-xylene with F₂TCNQ and F₄TCNQ, which produced poor crystals for the former and no crystals for the latter.

2.2. Crystallography

The X-ray diffraction data for the single crystals **1–4** (Table S1) were collected on a Bruker D8 Quest diffractometer. The programs used were APEX3 [26] for data collection, SAINT [27] for data reduction, SADABS [28] for multi-scan absorption correction, SHELXT [29] for structure solution and SHELXL [29] for structure refinement by full-matrix least squares against F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at carbon atoms were placed in calculated positions and refined as “riding” atoms. Crystal **4** exhibits the disorder of the fluorine atoms over four positions with different occupancies. In the centrosymmetric space group $P2_1/c$, the F_1 TCNQ molecule is in a special position on a crystallographic center of symmetry. Thus, it was refined in a space group Pc to give the occupancies equal to 0.34, 0.45, 0.13 and 0.08. CCDC 2295403–2295406 contain supplementary crystallographic data for this paper.

2.3. Quantum Chemical Calculations

Quantum chemical calculations were performed using the Gaussian 16 software package [30]. Full geometry optimization was carried out within the DFT method with the PBE0 and wB97XD functionals, as well as at the MP2 level of theory. In all cases, the 6-31+G(d) basis sets were employed in the calculations. BSSE corrections were performed using the counterweight method [31]. The energy of intermolecular interactions was calculated as the sum of energies of components minus the energy (BSSE corrected) of the supramolecular associate.

The interaction energy per one acceptor molecule was estimated using the Espinosa equation [32], and the electron potential energy density v_b at bond critical points (BCP) was calculated in frames of the Quantum Theory of Atoms in Molecules (QTAIM) [33].

3. Results and Discussion

A series of cocrystals of weak donor molecules, *o*-xylene, and *p*-xylene with fluorine-substituted TCNQ derivatives as acceptors were obtained by slow evaporation of solutions. The cocrystals are composed of mixed donor–acceptor stacks and have various (D:A) stoichiometry, which does not depend on crystal growth conditions. The studied systems involve the following donor and acceptor components with 1:1 and 2:1 ratios:

- *o*-xylene/ F_1 TCNQ (D:A = 2:1) (**1**);
- *o*-xylene/ F_2 TCNQ (D:A = 1:1) (**2**);
- *o*-xylene/ F_4 TCNQ (D:A = 2:1) (**3**);
- *p*-xylene/ F_1 TCNQ (D:A = 1:1) (**4**).

When going from benzene to its methyl-substituted derivatives, significant changes are observed, though donor properties of the molecules do not vary significantly. Only one cocrystal is reported for benzene with TCNQ derivatives [19]. The introduction of the methyl group to benzene increases the donor properties of the molecule just enough for toluene to form cocrystals with face-to-face 1:1 mixed stacks. However, the π - π interactions are so weak that the components in the stacks are not parallel [24]. The introduction of the second methyl group in xylenes increases the donor properties further and also brings unexpected changes in the stoichiometry in cocrystals. Toluene systems with F_1 -, F_2 - and F_4 TCNQ acceptors reported in our previous publication [24] all have 1:1 donor–acceptor ratio in cocrystals, while in the case of *o*-xylene, a 2:1 composition is observed for cocrystals **1** and **3**. Another outcome of the presence of the second methyl group is the fixed relative orientation of donor molecules within the stacks, while toluene in cocrystals is mostly disordered.

3.1. Crystal Structure of the Cocrystals **1–4** in Comparison with Toluene Cocrystals

o-Xylene forms 2:1 cocrystals with F_1 TCNQ with alternating D-D-A-D-D-A stacks and a layered structure with layers consisting of donor molecules alternating with layers of acceptor molecules (Figure 1). Donor and acceptor molecules within the stacks show an overlap of the benzene ring of the donor over the exocyclic double bond of the TCNQ

derivative. One of the methyl groups of the xylene molecules is located between the cyano groups. The second methyl group is close to the eclipsed position relative to the cyano group. Two neighbouring *o*-xylene molecules within the stacks are related by the inversion centre (Figure 1a). The relative orientation of the donor and acceptor molecules within the stacks is completely different from that in the toluene/ F_1 TCNQ cocrystal. In the latter, the stacks are irregular with the donor molecules above and below the acceptor molecules, exhibiting different respective orientations: one donor is located at a distance larger than the sum of the van der Waals radii with no overlap, and the second donor molecule has a ring over the endocyclic double bond overlap.

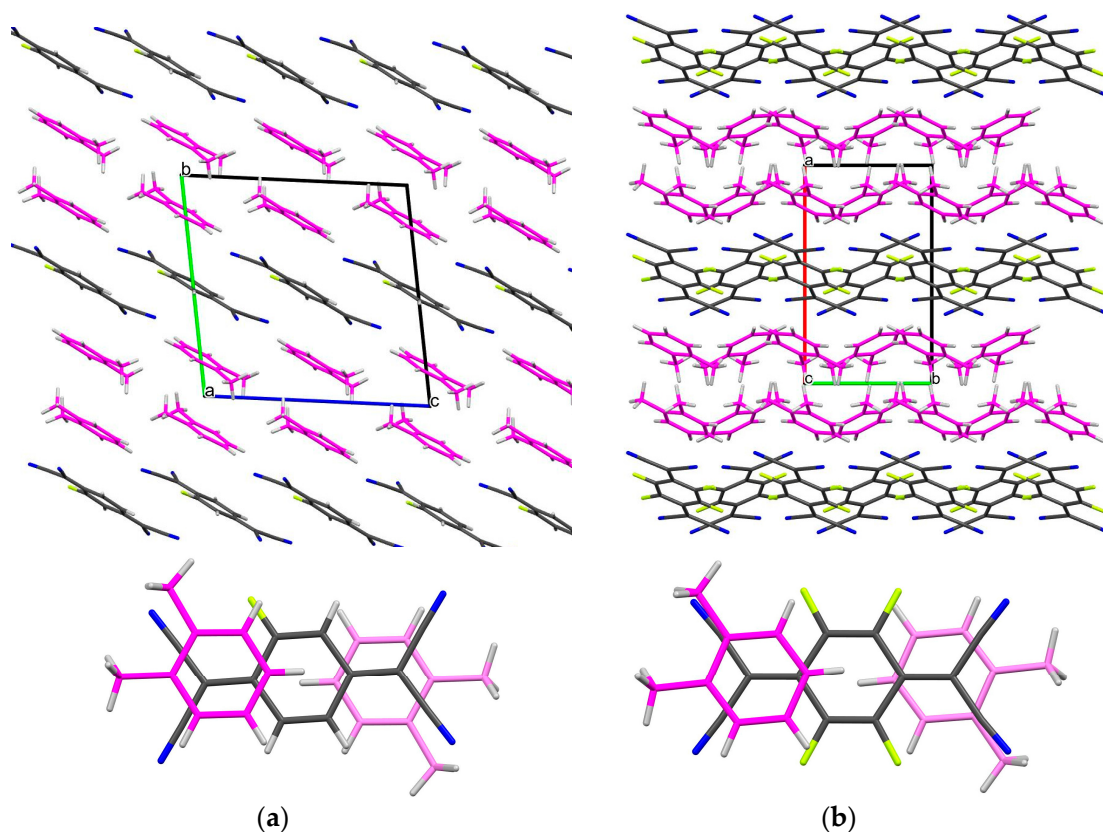


Figure 1. Fragments of crystal packing and the unit cells of cocrystal of (a) *o*-xylene/ F_1 TCNQ (2:1) (1) and (b) *o*-xylene/ F_4 TCNQ (2:1) (3) showing D-D-A mixed stacks arranged in layers (top) and the arrangement of molecules within the stacks (bottom).

The D-A overlap mode in the cocrystal of *o*-xylene with F_4 TCNQ is very similar to that in cocrystal 1 (Figure 1b). A similar layered structure and the same D:A ratio is observed; however, the molecules in the layers follow the herringbone motif. Unlike cocrystals with F_1 TCNQ, the same overlap mode is observed in the cocrystals of *o*-xylene and toluene with F_4 TCNQ, most probably owing to the stronger acceptor properties of F_4 TCNQ.

Unlike cocrystals 1 and 3, an equimolar D:A ratio is observed in cocrystals 2 and 4 obtained in the similar crystal growth conditions, but in the series of *o*-xylene complexes, only cocrystal 2 with F_2 TCNQ has a donor–acceptor ratio of 1:1 (Figure 2). A reasonable explanation might be in the comparatively strong hydrogen bonding between the acceptor molecules. This interaction between the cyano groups and hydrogen atoms results in infinite planar ribbons in cocrystal 2 (Figure 3a). The spare cyano group forms hydrogen bonds with donor molecules also located in the same plane. Such a planar hydrogen-bonded motif is preorganized for $\pi \cdots \pi$ interactions with the neighbouring ribbons. In contrast, there are no hydrogen atoms in the F_4 TCNQ acceptor; thus, no planar supramolecular arrangement is observed, and the acceptor molecules are located at approximately 33° with respect to each other (Figure 3b). A similar arrangement is observed in cocrystal 1 due to

the disorder of the fluorine atoms over four positions in F₁TCNQ. Such a supramolecular arrangement promotes a 2:1 donor–acceptor ratio.

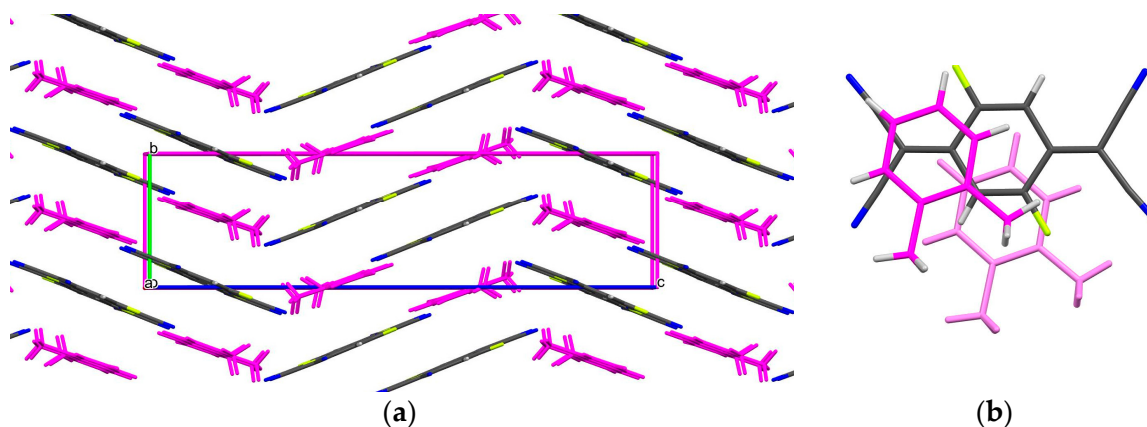


Figure 2. Fragments of crystal packing of cocrystal of (a) *o*-xylene/F₂TCNQ (1:1) (2) showing D-A mixed stacks with herringbone arrangement and the unit cell and (b) the D-A overlap within the stacks.

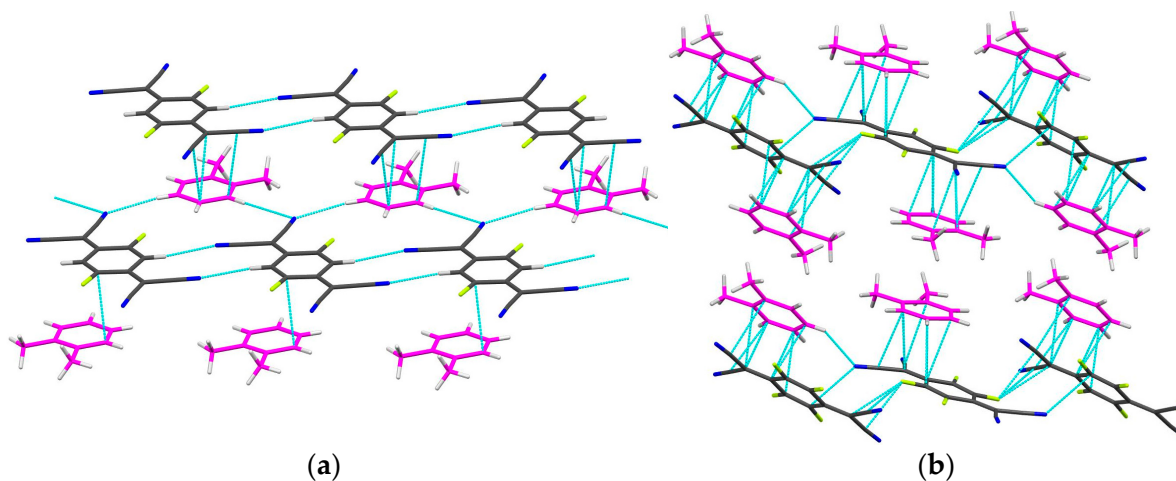


Figure 3. Fragments of crystal packing of cocrystal of (a) *o*-xylene/F₂TCNQ (1:1) and (b) *o*-xylene/F₄TCNQ (2:1) showing intermolecular short contacts (blue lines) in cocrystals.

p-Xylene forms cocrystal **4** with F₁TCNQ with the donor–acceptor ratio of 1:1. Cocrystal **4** has a very similar relative orientation, of the neighbouring donor and acceptor molecules in the stacks (Figure S1), as cocrystal **3**.

It should be noted that all cocrystals of F₁TCNQ exhibit the positional disorder of the fluorine atom over four positions. The xylene molecules in cocrystals are not disordered, while several types of disorder are observed in cocrystals of toluene (Figure 4). In cocrystal toluene/F₁TCNQ, three positions of toluene have slightly different orientations with respect to the acceptor molecule. In the cocrystal toluene/F₂TCNQ, whole-molecule disorder is observed, while in the cocrystal toluene/F₄TCNQ, the methyl group is disordered over two positions related by the inversion centre.

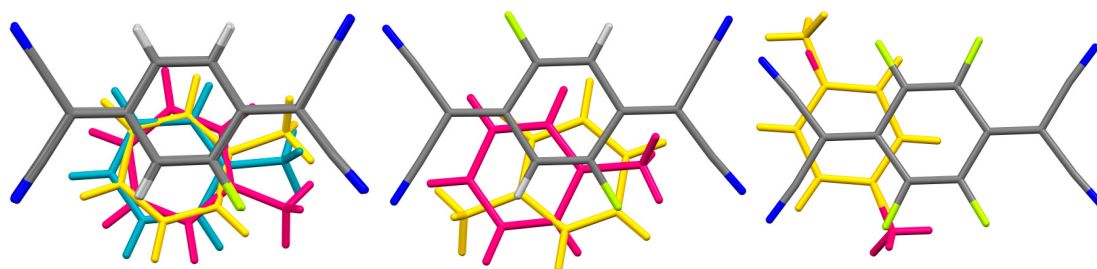


Figure 4. Fragments of crystal packing showing disorder of the toluene donors in cocrystals of toluene with F₁-, F₂- and F₄TCNQ (from left to right).

Thus, the structural data for the cocrystals of methyl-substituted benzenes with the TCNQ derivatives reveal several trends:

- The introduction of the two methyl groups into the benzene molecule significantly changes the relative orientation of the donor and acceptor molecules within the stacks and results in the formation of 2:1 donor–acceptor cocrystals with F₁TCNQ and F₄TCNQ in comparison to a 1:1 ratio for complexes of toluene.
- All toluene cocrystals exhibit disorder of the donor molecule, while in xylene cocrystals, two methyl groups fix the position of the donor within the stacks.
- The number of fluorine atoms in the acceptor molecule significantly changes the intermolecular interactions between acceptor molecules; in the case of F₁TCNQ cocrystals, fluorine atoms are in most cases disordered over all four possible positions due to their small volume.

3.2. The Analysis of Intermolecular Interactions in the Complexes of Xylenes Using Quantum Chemical Calculations

The crystal structure of the obtained series of cocrystals is determined by a plethora of weak intermolecular interactions; thus, even small changes in the structure of donor and acceptor molecules can produce drastic changes in the supramolecular structure of cocrystals. In order to understand the role of methyl substitution in donor components and the fluorine substitution in acceptor cofomers, we made a quantum chemical estimate of their donor and acceptor properties and the modelling of pairwise interactions in these cocrystals. The studied crystal structures involve several repeatable supramolecular synthons: donor–acceptor face-to-face synthons, *o*-xylene dimers in 2:1 cocrystals and hydrogen-bonded acceptor–acceptor planar dimers in F₂TCNQ cocrystals. The analysis of these pairs may help to determine the rating of intermolecular interactions in these cocrystals and explain the variable stoichiometry of components. In the title systems the introduction of the second methyl group into the donor may increase the interaction of these molecules with each other due to the enhancement of π -stacking dispersion interactions. However, these interactions are not properly captured within the framework of the DFT method using conventional hybrid functionals. Therefore, in addition to the widely used PBE0 functional, the wB97XD functional with empirical dispersion corrections was applied. However, dispersion corrections should be system-dependent in order to obtain accurate results for aromatic interactions [34]. Unfortunately, such corrections have been validated only on a limited number of systems. Therefore, in some cases, benchmarking calculations were carried out at the MP2 level of theory.

Overall, xylenes are stronger donors than toluene [35], and the HOMO values (Table S2) are in full agreement with this. At the same time, the HOMO energy values slightly increase in the series of *ortho*-, *meta*- and *para*-derivatives.

3.2.1. The Analysis of Charge-Transfer D-A Pairs

The DFT calculations of donor–acceptor pairs with a face-to-face supramolecular arrangement show two energy minima with a benzene ring of xylenes over the exocyclic (*exo*-overlap) or endocyclic (*endo*-overlap) double bonds of the TCNQ derivatives (Figure 5).

The PBE0 functional slightly favours the *exo*-overlap mode, while in view of the wB97XD functional, the *endo*-overlap mode is more favourable (all data can be found in Table S3, some essential data are collected in Table 1). For each overlap there are several isomeric dimers with different orientations of fluorine atoms and methyl groups, which are very close in energy scale.

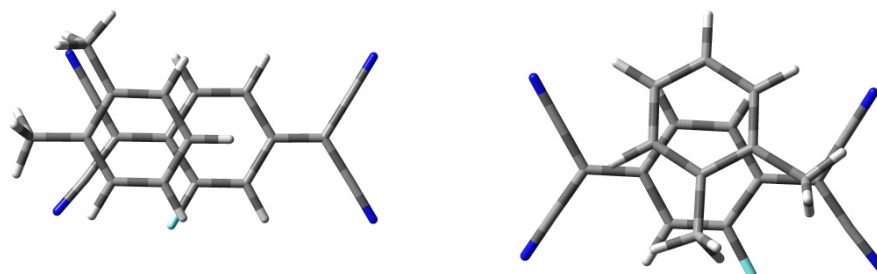


Figure 5. Two face-to-face supramolecular arrangements with *exo*- and *endo*-overlaps.

Table 1. The energy of intermolecular pairwise interactions and interplanar distances for some representative dimeric complexes based on optimizations by different methods (6-31+G(d)).

Dimer	PBE0		wB97XD		MP2	
	d (Å)	E (kcal/mol)	d (Å)	E (kcal/mol)	d (Å)	E (kcal/mol)
<i>o</i> -xylene/TCNQ *	3.794	2.98	3.320	11.20	3.211	9.27
<i>o</i> -xylene/F ₁ TCNQ	3.681	3.47	3.332	12.08	3.178	10.23
<i>o</i> -xylene/F ₂ TCNQ	3.633	3.78	3.265	12.53	3.154	10.81
<i>o</i> -xylene/F ₄ TCNQ	3.522	4.61	3.242	13.80	3.155	12.52
<i>m</i> -xylene/TCNQ	3.709	2.86	3.322	12.09		
<i>m</i> -xylene/F ₁ TCNQ	3.635	3.18	3.289	12.45	3.184	10.24
<i>m</i> -xylene/F ₂ TCNQ	3.618	3.45	3.284	12.83		
<i>m</i> -xylene/F ₄ TCNQ	3.562	4.49	3.252	14.19		
<i>p</i> -xylene/TCNQ	3.797	2.80	3.339	12.43	3.233	9.82
<i>p</i> -xylene/F ₁ TCNQ	3.685	3.37	3.316	13.32	3.198	10.78
<i>p</i> -xylene/F ₂ TCNQ	3.668	3.55	3.313	13.56	3.186	11.19
<i>p</i> -xylene/F ₄ TCNQ	3.556	4.43	3.285	14.84	3.143	12.86
<i>o</i> -xylene/ <i>o</i> -xylene **	3.919	1.52	3.471	8.23	3.413	4.83
<i>m</i> -xylene/ <i>m</i> -xylene	3.929	1.19	3.295	6.89	3.314	3.91
<i>p</i> -xylene/ <i>p</i> -xylene	3.945	1.20	3.481	6.34	3.456	3.72
F ₁ TCNQ/F ₁ TCNQ	2.406 ***	5.62	2.447	7.33	2.495	6.50

* dimers with *exo*-overlap; ** dimer CH/π di-stack; *** N...H hydrogen bond distances.

It is noteworthy that, quantitatively, the wB97XD functional predicts a noticeably stronger stabilization energy for such CT complexes as well as shorter distances between the aromatic D-A planes relative to PBE0 results. At the same time, the comparison of the values obtained for several F_xTCNQ/xylene pairs reveals that the energy obtained within the wB97XD approach is 25–30% larger than the energy calculated at the MP2 level. It follows that the wB97XD functional leads to a strong overestimation of the energy of CT interactions, although the distances between the planes of the cycles are reasonable.

Addressing the fine details (Table S3), in particular the energy dependence on the isomeric structure of xylene, one can see that two functionals give slightly different trends. Specifically, the PBE0 functional produces the largest interaction energy for *o*-xylene and the smallest energy for *meta*-derivative. At the same time the wB97XD functional gives increasing energy in the series of *ortho*- and *meta*- with the maximal energy for *para*-xylene.

Considering the trend for the series of donors, benzene–toluol–xylene, the stabilization energy increases by 0.4–0.5 kcal/mol (PBE0) for each additional methyl group, while the fluorine substitution results in 1.6 kcal/mol stabilization of F₄TCNQ in comparison to unsubstituted acceptor TCNQ.

3.2.2. The Analysis of Donor–Donor Interactions

The principal difference between toluene and xylene cocrystals with the TCNQ derivatives is the 2:1 donor–acceptor ratio in two cocrystals of *o*-xylene versus the 1:1 ratio in cocrystals of toluene. To obtain an insight into the reasons behind this, donor–donor face-to-face interactions were analysed for three structural motifs, involving π – π stacking interactions between the rings (π -stack) (Figure 6a), $\text{CH}\cdots\pi$ interactions with the participation of two methyl groups (CH/π di-stack) (Figure 6b) and $\text{CH}\cdots\pi$ interactions with the participation of only one methyl group (CH/π mono-stack) (Figure 6c). These dimers are shown for *p*-xylenes. Two functionals give different estimates for the stability of these structural isomers (Table S4). According to PBE0 calculations, π -complexes do not correspond to an energy minimum, as is expected for this functional. CH/π mono-stack dimers are also not stable in most cases. The only stable isomer is CH/π di-stack: its stabilization energy grows in the series of *para*- and *meta*- and is maximal for *ortho*-xylene dimers.

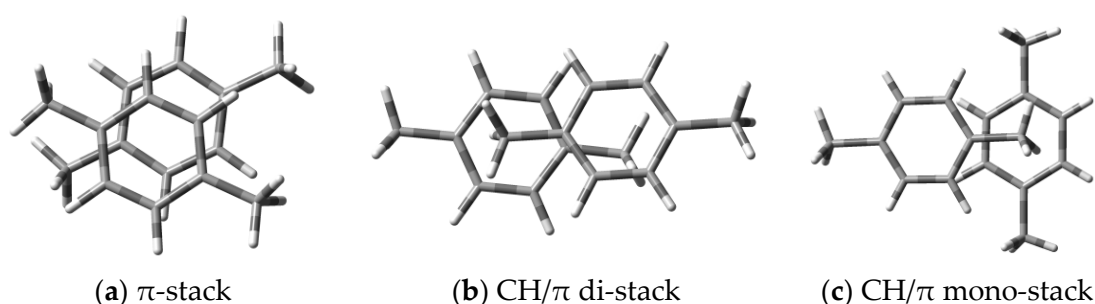


Figure 6. Possible structural motifs of *p*-xylene according to DFT calculations.

At the same time, the wB97XD functional gives an energy minima for the CH/π mono-stack and sometimes π -stack supramolecular arrangements with the energy difference being small.

The general trend observed for both functionals is the larger stability of the CH/π di-stack dimer for *o*-xylene. This fact explains the formation of 2:1 donor–acceptor cocrystals 1 and 3 for *o*-xylene. It is important that the relative orientation of *o*-xylene/*o*-xylene pairs is the same in both cocrystals (Figure 7a) in spite of the overall different crystal packing. This observed geometry is very close to the relative orientation obtained in light of DFT calculations (Figure 7b).

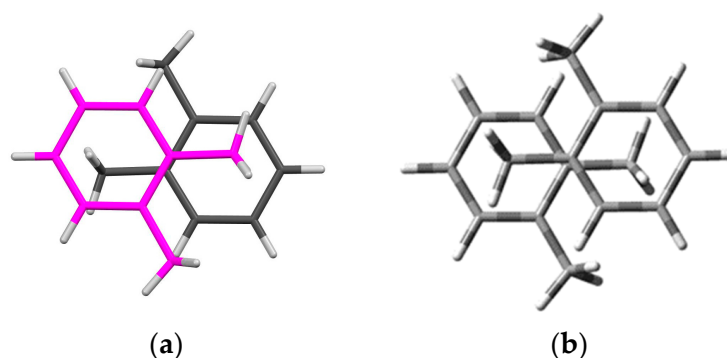


Figure 7. Relative orientation of *o*-xylene pairs in cocrystals 1 and 3 (a) and optimized geometry (b).

For D–D interactions, the DFT-wB97XD approach produces similar results as those for D–A complexes: the aromatic rings are significantly closer and the interaction energy is much larger than that obtained with the PBE0 functional. However, it seems that the empirical correction taking into account dispersion interactions implemented in the wB97XD functional, results in its significant overestimation. In particular, it is 1.52 versus 8.23 kcal/mol for *o*-xylene, respectively, for the PBE0 and wB97XD functionals. Calculations at the MP2 level of theory for several CH/π di-stack xylene complexes confirm this assump-

tion. The “MP2 energies” are ~3.5 kcal/mol smaller than the wB97XD results. Thus, since MP2 is known to overestimate [36] the energy of π - π interactions between the aromatic rings, it is most probable that DFT-wB97XD calculations double the complexation energy.

It is interesting to verify this premise using a more simple model—toluene. In view of the DFT-PBE0 approach, CH/ π di-stack, CH/ π mono-stack and T-shape isomers correspond to the energy minima. According to the MP2 and DFT-wB97XD methods, the π - π stack is also a stable structure, which is in good agreement with the results for xylenes. At the same time, the wB97XD functional does not produce an energy minimum for the classical T-shaped complex (Table S5). In general, it is evident that the wB97XD functional gives larger values for the interaction energy in this complex in comparison to MP2 data.

To conclude, taking into account that MP2 calculations somewhat overestimate the energy of dispersion interactions [36], we can assume that the DFT-wB97XD method gives an even larger overestimation; thus, these results should be used with care, especially in the case of classical aromatic π - π complexes.

3.2.3. The Analysis of Acceptor–Acceptor Lateral Interactions

DFT calculations using both functionals reveal significant lateral intermolecular interactions in some acceptor–acceptor pairs (Table S6). The F₄TCNQ acceptor does not show an energy minimum for lateral intermolecular interactions. The maximal energy of the hydrogen bonding CN...H is observed in F₁TCNQ pairs, followed by TCNQ and further by F₂TCNQ. Absolute values for stabilization energy obtained in light of both functionals are very close; moreover, the MP2 method gives similar values. Thus, both functionals can be used to estimate hydrogen bonding interactions in these systems.

3.2.4. The QTAIM Analysis of Intermolecular Interactions in Xylene Cocrystals

The energy of pairwise intermolecular interactions and the values of charge transfer in xylene cocrystals were estimated using the R. Bader QTAIM approach [33] for the experimentally observed geometries (Table 2). The energy values obtained using this approach are very similar to those from DFT-PBE0 calculations and are independent of the functional that has been used to obtain the wave functions. The values of charge transfer in these cocrystals do not exceed 0.08 e, which is reasonable for weak charge-transfer complexes, and changes in unison with the donor–acceptor distance.

Table 2. The energy of intermolecular interactions and charge-transfer values estimated by QTAIM approach based on wave functions obtained using two different functionals and experimental geometry.

Cocrystal	Contact	d (Å)	PBE0/6-31+G(d)		wB97XD/6-31+G(d)	
			E (kcal/mol)	ρ (e)	E (kcal/mol)	ρ (e)
1	D-A	3.250 (4)	3.33	0.053	3.33	0.042
	D-D	3.566 (4)		3.33	3.33	
	D-D	3.734 (4)		2.67	3.29	
2	* D-A	3.402 (3)	2.73	0.035	2.76	0.032
	** D-A	3.309 (2)	2.70		2.73	0.041
3	D-A	3.348 (3)	2.98	0.085	3.01	0.063
	D-D	3.672 (4)	2.98		2.98	
4	D-A	3.342 (4)	4.05	0.039	4.05	0.031

* endocyclic and ** exocyclic overlap modes in irregular stacks.

4. Conclusions

A series of weak CT cocrystals was obtained with *o*- and *p*-xylene as donors and fluorine-substituted TCNQ derivatives as acceptors. Unlike toluene complexes with the same acceptors, which all form 1:1 cocrystals with mixed donor–acceptor stacks, *o*-xylene forms 2:1 cocrystals with F₁- and F₄TCNQ in the same crystal growth conditions, owing to C-H... π attractive interactions between the donor molecules. Two methyl groups in xylene

donors serve as anchors, which fix donor molecules within the stacks, thus preventing disorder, which is typical for toluene cocrystals.

The analysis of pairwise donor–acceptor interactions by quantum chemical methods reveals two molecular overlap modes, which are very close in energy and which correspond to the energy minima with the benzene ring of the donor located either over the exocyclic or endocyclic double bond of the TCNQ. Both modes are reproduced in the cocrystals. The overall crystal packing is determined by the acceptor molecules due to the small size of the donor and strongly depend on the number of fluorine atoms in the acceptor. In the case of F₁TCNQ, the fluorine atom is disordered over all four possible positions in all cocrystals.

Pairwise interactions were examined for donor–acceptor and donor–donor face-to-face pairs as well as for acceptor–acceptor C $\cdots$ H hydrogen bonding interactions, which play an important role in crystal packing. The energy of face-to-face interactions was found to depend predictably on the DFT functional being much larger for wB97XD than for PBE0. The inclusion of dispersion interactions produces the geometry of donor–acceptor and donor–donor dimers, which is very close to the arrangement observed in cocrystals. The PBE0 functional gives proper mutual orientation of the molecules in pairs but a significantly larger interplanar distance. To verify the applicability of the wB97XD functional for such supramolecular systems, the MP2 approach was used, which allowed us to conclude that the DFT-wB97XD calculations strongly overestimate the energy of interactions in these charge-transfer systems.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cryst13101515/s1>: Crystallographic data for the studied cocrystals (Table S1); Figure S1 showing crystal packing in *p*-xylol/F₁TCNQ cocrystal; and Tables S2–S6 summarizing the results of quantum chemical calculations for pairwise interactions within different approaches.

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